HIGH POWER ENERGY CONVERSION
IN
P-N SEMICONDUCTOR JUNCTIONS

by

JOHN DANIEL RICHARDSON, JR.

COURSE XIII-A

22 May 1964

HIGH POWER ENERGY CONVERSION
IN
P-N SEMICONDUCTOR JUNCTIONS

by

JOHN DANIEL RICHARDSON, JR.

B.S., U.S. Naval Academy

(1957)

SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE PROFESSIONAL DEGREE OF
NAVAL ENGINEER
AND FOR THE DEGREE OF
MASTER OF SCIENCE
IN
ELECTRICAL ENGINEERING
at the
MASSACHUSETTS INSTITUTE OF TECHNOLOGY

June, 1964

HIGH POWER ENERGY CONVERSION
IN
P-N SEMICONDUCTOR JUNCTIONS

by

JOHN DANIEL RICHARDSON, JR.

Submitted to the Department Naval Architecture and Marine Engineering and the Department of Electrical Engineering on 22 May 1964 in partial fulfillment of the requirements for the professional degree of Naval Engineer and the degree of Master of Science in Electrical Engineering.

ABSTRACT

Methods of reducing sheet resistance are reviewed and investigated to determine which one has particular application in the thermo-photo-voltaic cell. The reduction of sheet resistance by the deposition of a transparent conducting overlay on the incident face of the TPV cell is considered from a theoretical analysis using thin film calculations and optical parameters of various semi-conducting materials. It is shown as a result of the calculations that thin films applied to TPV cells can produce an increase in conversion efficiency. To assist the theoretical investigation of thin film materials, an index is defined and normalized against the properties of highly doped germanium. Values for the index determine the suitability of materials for overlay application.

Thin films of tin dioxide can be deposited by pyrolytic action or reactive cathodic sputtering techniques. The sputtering process is shown to possess suitable properties for overlay application on germanium substrates. An experimental program is outlined which would substantiate the assumption in the theoretical investigation.

Thesis Supervisor: Bruce Daniels Wedlock

Title: Assistant Professor of Electrical Engineering

ACKNOWLEDGEMENTS

The author wishes to thank his thesis supervisor, Professor Bruce D. Wedlock for the many helpful suggestions during the course of this investigation and for his help in preparing this manuscript. He also would like to thank Professor James G. Gottling of the Electronics Systems Laboratory for providing vacuum deposition facilities. Numerical calculations of this thesis were done in part at the Computation Center at the Massachusetts Institute of Technology, Cambridge, Massachusetts.

TABLE OF CONTENTS

CHAPTER I THEORETICAL CONSIDERATIONS AND SERIES RESISTANCE

CHAPTER II THEORETICAL CALCULATIONS

CHAPTER III EXPERIMENTAL INVESTIGATION

CHAPTER IV SUGGESTIONS FOR FUTURE WORK

LIST OF TABLES

LIST OF ILLUSTRATIONS

CHAPTER I

THEORETICAL CONSIDERATIONS AND SERIES RESISTANCE

1.1 Introduction

The central theme of any technological development includes the assumption that an energy source is available to assist the program in its implementation. Energy is available to man in many forms, but one of the limitations of nature is that this energy is not available for direct application to most of the needs of a modern society and certainly not for an expanding technology. Hence, natural energy sources must be converted to forms which will readily aid man in his continuing desire for advancement. Electrical energy at the present time is the most desirable form of energy to aid this progress, but electrical energy does not occur for man to use directly. Thus, some form of conversion process must be used to change what is available into electrical energy. The largest available sources produce thermal energy as a result of some reaction, e.g., chemical or nuclear. The conversion of this thermal energy can be either direct or indirect. This paper will deal with a direct process, as used by the thermo-photo-voltage (TPV) converter, in which thermal radiation from an incandescent body is converted to electrical energy in

a semiconductor. The thermo-photo-voltaic convertor is outlined in detail in White, et al, (1)* and Wedlock (2).

1.2 Background

Conversion of thermal radiant to electrical energy by a P-N junction is made possible by an efficient electron-photon interaction in which incident photons having energy equal to or greater than the semiconductor bandgap are absorbed. This absorption produces hole-electron pairs that are subsequently separated by the built-in field at the junction. The resultant junction photovoltage is the difference between the junction contact potential at thermal equilibrium and the total junction potential under photon irradiation. An external open circuit voltage appears at the terminals of the junction diode as a result of a required change in junction barrier height. This voltage, when suitable electrical connections are made, will cause an electrical current to flow in the external circuit. The carriers comprising this current are the electrons and holes generated under photon irradiation as minority carriers in the respective P and N type materials. The current in the external circuit is proportional to the number of photons absorbed. The voltage depends on several factors including the type of semiconductor and the doping level

---

*Numbers in parentheses refer to items in the references.

of the P and N regions, as these and other factors influence the barrier height.

Energy converted in the diode under photon irradiation can be lost in internal dissipation arising from resistive losses. The following resistance components are present in the TPV cell: sheet resistance of the diffused layer, bulk resistance of the semiconductor substrate and contact resistance to the P and N type regions. It is sheet and contact resistances to which the remainder of this paper will be devoted.

The sheet and contact resistances are collectively called the series resistance which greatly affects the ultimate conversion efficiency. For a typical model of a thermo-photo-voltaic converter containing a shunt and series resistance, the I-V characteristic is given by:

$$\ln\left[\frac{I + I_L}{I_o} - \frac{V - IR_S}{I_o R_{SH}} + 1\right] = \frac{q}{kT}(V - IR_S). \quad \text{(I-1)}$$

The theoretical I-V characteristic obtained from plotting this equation for a range of series and shunt resistances shows that shunt resistance is not important.(3) Figure I-1 shows the effect of various series resistances on the theoretical I-V characteristics. Figure I-2 illustrates the effect of series resistance on the maximum power available from a cell. Thus it is apparent that series resistance should be reduced to as low a value as possible.

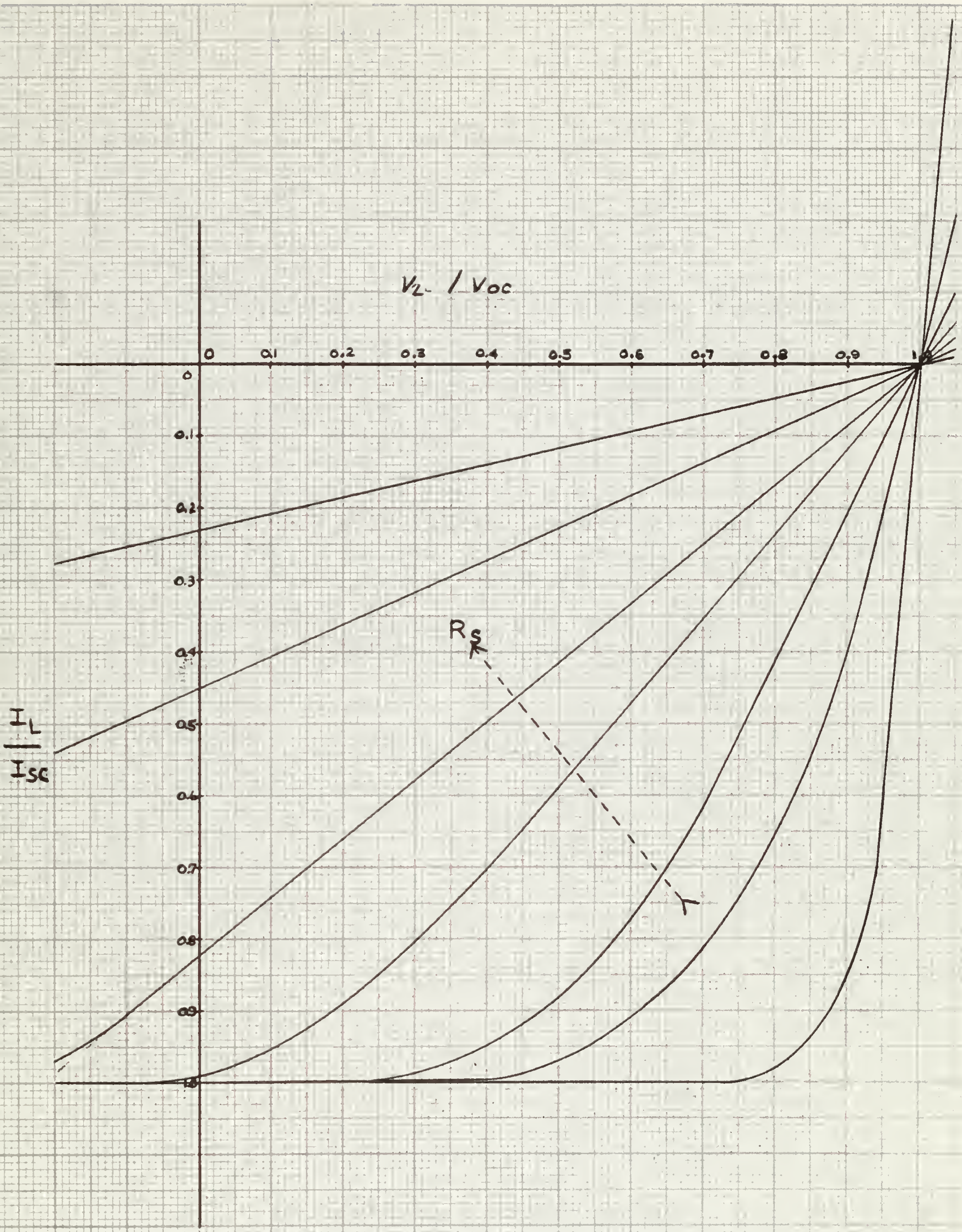
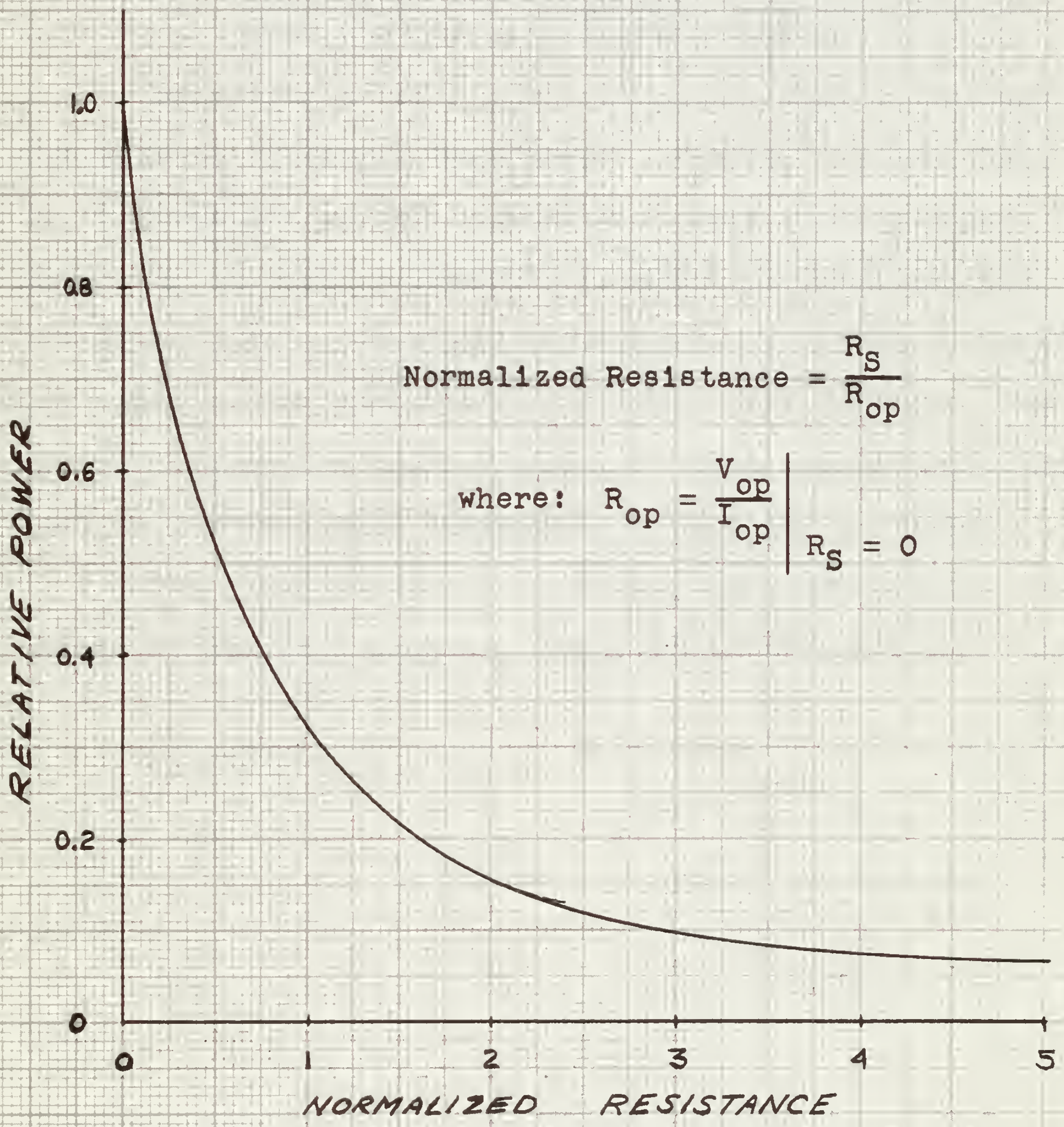


Figure I-1. Normalized Theoretical I-V Characteristics for Various Converters with Different Series Resistances



$$\text{Normalized Resistance} = \frac{R_S}{R_{op}}$$

$$\text{where:} \quad R_{op} = \left.\frac{V_{op}}{I_{op}}\right|_{R_S = 0}$$

Figure I-2. Relative Available Power as a Function of Normalized Series Resistance

Schemes that have been proposed for the reduction of series resistance are as follows:

(a) Proper selection of cell geometry.

(b) Highly doping the diffused incident layer.

(c) Gridding of cell diffused incident layer.

(d) Application of transparent conducting layer over the diffused incident layer.

Selection of cell geometry can be used to decrease the effects of series resistance. Prince(3) shows that for a given set of cell parameters there is an optimum shape for the cell. Prince's remarks are pertinent for the silicon solar cell in particular, but only in a general way apply to the thermo-photo-voltaic cell; however, the general assumption that geometry of cell construction can lead to improved cell conversion efficiency is valid.

The geometry to be considered throughout this thesis is the cell geometry depicted in Figure I-3.

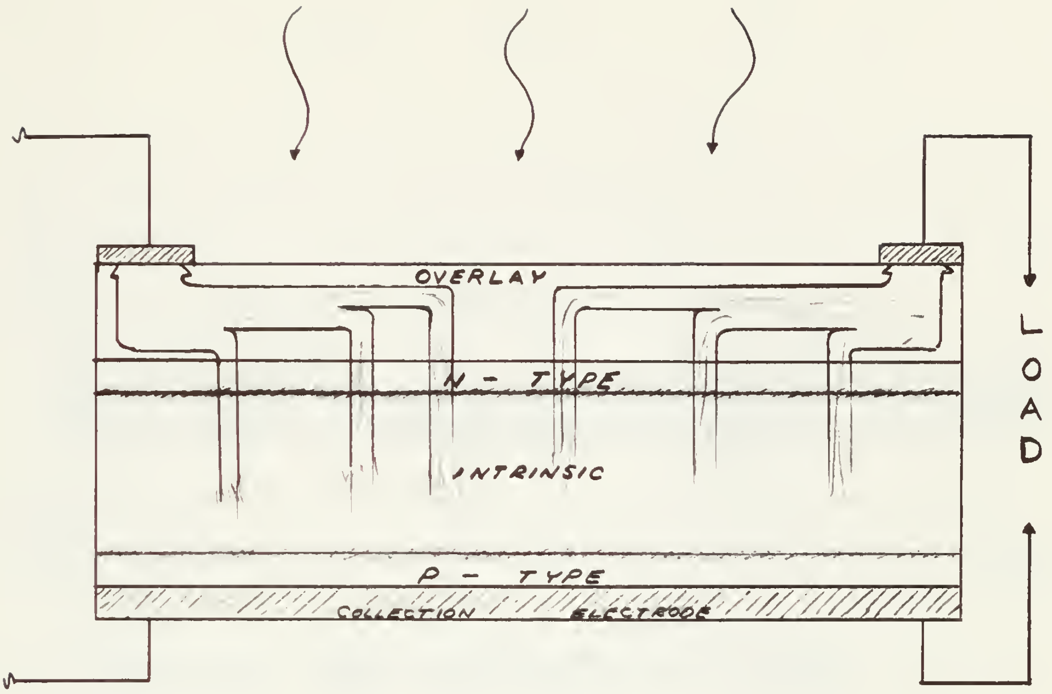


Figure I-3 CELL GEOMETRY

Some geometrical arrangements have been considered which will lessen the effect of sheet resistance, for example the edge illuminated P-I-N device depicted in Figure I-4. The bulk resistance under radiation of the active semiconductor in devices of this nature becomes the important component of series resistance. Geometries of the type in Figure I-4 will not be discussed in this thesis.

[illegible]

[illegible]

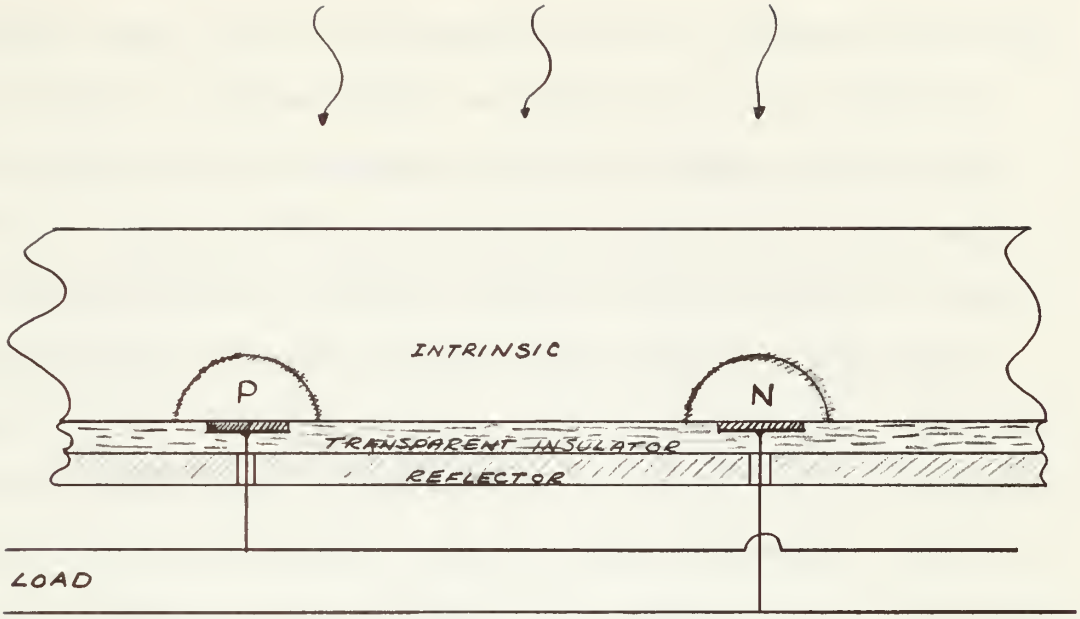


Figure I-4 EDGE ILLUMINATED P-I-N CELL

Heavy doping of the incident layer aids in reduction of series resistance by lessening the sheet resistance. The disadvantage of this technique is that highly extrinsic material generally has a low lifetime which affects both the diffusion length and the density of optically generated carriers. The mobility also decreases as the number of impurities increases. The combined effect is to reduce the diffusion length in extrinsic germanium, for example, by a factor of 10 to 100 over that of intrinsic germanium. The absorption coefficient in germanium rapidly increases in the region of photon energies slightly above that of the gap energy, such, that at a wave length of 1.5μ the absorption coefficient is close to 10^4 centimeters^{-1}. This increased absorption coefficient causes the hole-

electron pairs that are generated due to interactions with the photons at these higher energies to occur closer to the surface. The decreased diffusion length associated with the highly extrinsic material coupled with the surface generation of carriers results in an increase in the recombination of hole-electron pairs before separation occurs at the junction field. This recombination subtracts from the conversion efficiency of the cell. Thus for wavelengths that are shorter than the gap wavelength, the collection efficiency decreases in the heavily doped germanium.

Heavily doping the incident layer to reduce sheet resistance in a germanium cell on which a broad band of radiation is incident can result in a lessened efficiency. On the other hand, if the cell were to be subjected to a very narrow band of radiation, then the junction could be placed at an optimum depth. Overall conversion efficiency would be increased for this situation since the generation of hole-electron pairs could be made to occur in an area very close to the junction. The same effect will take place in a material having an absorption coefficient which is relatively constant over the spectrum of the incident radiation.

The use of gridding is a variation of cell geometry in which the cell is divided into a large number of parallel units. The disadvantage of gridding is that the collection electrodes mask the incident face and reduce the area of active material available for conversion. The employment

of gridding to increase conversion efficiency and power density has been successfully utilized in silicon solar cell technology.

It appears that grids will be effective in increasing the conversion efficiency of TPV cells under high levels of illumination. Reflection from the grids on the cell face will not be lost to the system because in the projected TPV convertor geometry, this reflected radiation would be returned to the source.

Application of a highly transparent conducting overlay on the incident diffused face would aid in increasing cell efficiency by reduction in the series resistance if:

(a) The transparency of the overlay were very good in the bandlimited radiation used for the converter,

(b) The conductivity of the overlay were very high and

(c) The overlay were to make an ohmic contact to the semiconductor substrate.

The selection of a material to meet the above criteria is not simple. The requirement that a material be conducting to electric currents also means, on classical terms, that it not be transparent to electromagnetic energy.

1.3 Material Considerations

Electrical conduction in a metal can be attributed to the high concentration of free conduction electrons. It is these electrons which make the metals so highly absorptive

to radiant energy. In a material that has the properties of a semiconductor, the concentration of free electrons is less, and therefore absorption by this mechanism is more limited. However, in a semiconductor the main contributors to absorption are from bound electrons and electrons undergoing transitions from the valence band to the conduction band, thereby causing the absorption characteristics for a semiconductor to be different from a metal. The optical constants of a number of semiconductors have been measured over a wide range of wavelengths. The characteristic feature of all semiconductors, in the pure state, is that at a certain wavelength the absorption coefficient drops rapidly and the material becomes fairly transparent to longer wavelengths. Absorption at longer wavelengths in a semiconductor is due mostly to free carriers. The electrical conductivity in a semiconductor is proportional to free carrier concentration. By controlling this concentration it is thus possible to achieve a degree of control over the above listed overlay requirements.

Experimenters investigating the properties of thin deposits of metals obtained by vacuum evaporation discovered that some of the metallic films when very thinly evaporated exhibited optical transparency. Investigation into the electrical and optical properties of these films showed that the constants obtained departed from those of the bulk materials. The departure is attributed to the aggregated structure of the thin films. The thickness at which

a homogeneous layer develops on a substrate determines whether the film is thin enough to be both transparent and conducting. The production of a homogeneous film depends on the relation between the binding forces of the condensed atoms and the substrate and the cohesive forces in the film. The film will produce a homogeneous layer when the former are larger than the latter.(4) Thus thin metallic films exhibit properties which could make them useful for overlay application.

It is the primary intent of this thesis to analytically investigate the feasibility of utilizing certain semiconductors and thin metallic films as potential materials for overlay application.

1.4 Theoretical Considerations

A closer look into the feasibility of application of a transparent conducting overlay to the incident face of a TPV cell for reduction of sheet resistance is apparent. It is necessary to determine what materials, if any, might be best suited to this purpose.

The two factors which affect the determination of the overlay material are electrical conductivity to direct currents and optical transparency to the band of infrared energy which will be used in the cell for production of hole-electron pairs. An ideal material would be one which is

(a) Transparent to the band of energy,

(b) Reflect all photons with energies outside the band,

(c) Absorb none of the incident radiation and be

(d) A very good conductor.

No known material exists which can do all of the above, but there are some semiconducting materials which combine these criteria to varying degrees.

In order to be able to describe the properties of a given material for overlay application some factor must be defined which incorporates the optical transparency and electrical conductivity. Such a factor is the transparency-conductivity index defined as:

$$\psi = \sigma \, t \, T \tag{I-2}$$

where: ψ Transparency-conductivity index

t Film thickness in microns

σ Conductivity in mhos per centimeter

T External transmission of film.

The transmission of a film is dependent upon the thickness of the film, and to some extent for a very thin film so does the conductivity; however, it will initially be assumed that the films are sufficiently thick that bulk properties are applicable. This assumption is valid for thicknesses over 0.1 microns.(5,6)

A criterion upon which to base the usefulness of a given overlay material in reducing the sheet resistance might be to compare it with a cell that had a more highly doped and deeper diffused layer. It is apparent that attempts to reduce sheet resistance by this means in germanium cells can result in lowered conversion efficiency. The reason for the drop is that heavy doping in the extrinsic material decreases carrier lifetime and mobility; this reduction coupled with the large absorption coefficients for the higher energy photons will reduce the collection efficiency and cause the cell to produce electrical energy less efficiently. Thus this attempt to reduce sheet resistance is not effective from the overall standpoint of cell conversion efficiency; but, nonetheless, the technique of heavy doping and increasing diffused layer depth is available and in the TPV cell does improve efficiency due to the limited spectrum of the incident radiation, thus use of this method as a criterion for normalization of ψ is justified. Any overlay scheme that is to be considered must be more effective at reducing sheet resistance than increasing the doping level and the depth of the diffused layer, if not, then its use for this purpose is not justified.

The previously defined transparency-conductivity index can then be normalized with the above criterion in mind by defining:

$$\psi_N = \frac{\psi \text{ for overlay material}}{\psi \text{ for doped germanium}} \qquad \text{(I-3)}$$

Thus it is the normalized index that will be used to determine the relative effectiveness of a given material for overlay application. Materials which have a $\psi_N > 1$ will be examined more closely.

The question of contact resistance enters into the problem, but this particular approach will assume that for a first approximation the material will make an ohmic contact. The validity of this assumption will depend on which materials have values of $\psi_N > 1$ and the experimental results obtained from application of these materials on a semiconductor face.

CHAPTER II

THEORETICAL CALCULATIONS

2.1 Introduction

The effectiveness of various materials for overlay application as defined by the transparency-conductivity index requires that the optical transmission of a material as a function of wavelength be known. It is possible to calculate the external transmission of a thin film if the indicies of refraction and extinction are known as a function of wavelength, also values of transmission may be determined for varying thicknesses with these data.

To aid in the final selection of overlay materials, it would be informative to know the amount of reflection and absorption that any given film experiences since these two factors are important in the determination of cell conversion efficiency.

Absorption in the overlay material must be as low as possible otherwise the gain in efficiency through reduced series resistance occasioned by the overlay could be more than offset by the photon absorption in the applied film. It is desirable to know also the optical characteristics of the overlay for the entire spectrum to which the cell will be subjected because the properties of reflection, absorption and transmission to photons which do not produce photon-electron interactions in the active semiconductor

determine the desirability of an overlay for a particular application.

2.2 Thin Film Calculations

To calculate the transmission of a film that is in optical contact with a more massive substrate, the equations developed by Drude(7) were used. The geometry assumed in the derivation of Equation II-1 is depicted in Figure II-1. Both materials are assumed to be absorbing and the substrate is considered semiinfinite.

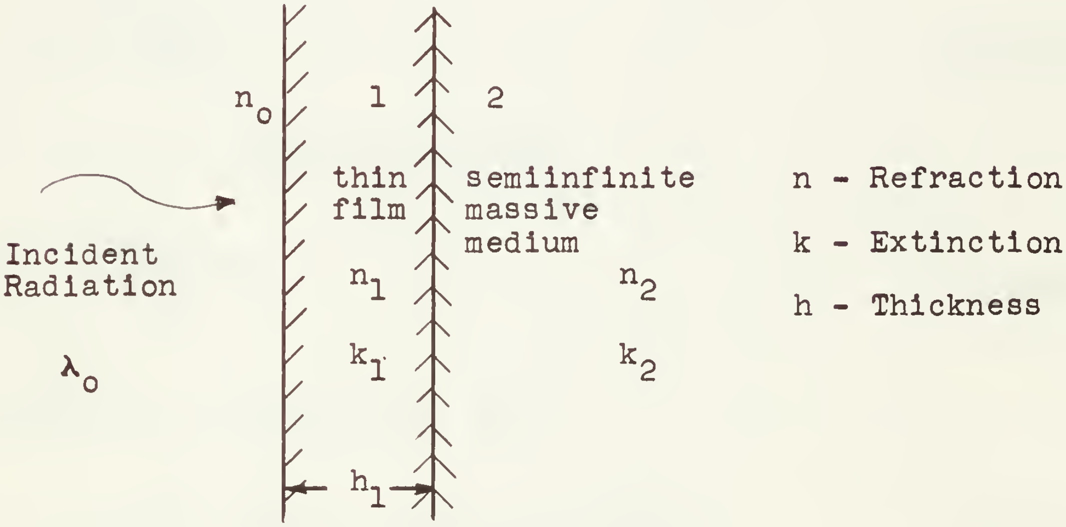


Figure II-1

The transmission is calculated from:

$$T = \frac{16\, n_o n_2 (n_1{}^2 + k_1{}^2)}{b_1 e^{\sigma} + b_2 e^{-\sigma} + b_3 \cos v + b_4 \sin v} \qquad \text{(II-1a)}$$

where:

$$b_1 = \left[(n_o+n_1)^2 + k_1{}^2\right]\left[(n_1+n_2)^2 + (k_1+k_2)^2\right] \qquad \text{(II-1b)}$$

$$b_2 = \left[(n_o-n_1)^2 + k_1{}^2\right]\left[(n_1-n_2)^2 + (k_1-k_2)^2\right] \qquad \text{(II-1c)}$$

$$b_3 = 2\left\{\left[n_o{}^2 - (n_1{}^2+k_1{}^2)\right]\left[(n_1{}^2+k_1{}^2) - (n_2{}^2+k_2{}^2)\right] - 4n_o k_1 (n_1 k_2 - n_2 k_1)\right\} \qquad \text{(II-1d)}$$

$$b_4 = 4\left\{\left[n_o{}^2 - (n_1{}^2+k_1{}^2)\right]\left[(n_1 k_2 - n_2 k_1)\right. + n_o k_1 \left[(n_1{}^2+k_1{}^2) - (n_2{}^2+k_2{}^2)\right]\right\} \qquad \text{(II-1e)}$$

$$\sigma = \frac{4\pi k_1 h_1}{\lambda_o} \qquad \text{(II-2a)}$$

λ_o = Vacuum wave length

$$v = \frac{4\pi n_1 h_1}{\lambda_o} \qquad \text{(II-2b)}$$

The reflection is calculated from:

$$R = \frac{a_1 e^{\sigma} + a_2 e^{-\sigma} + a_3 \cos v + a_4 \sin v}{b_1 e^{\sigma} + b_2 e^{-\sigma} + b_3 \cos v + b_4 \sin v} \qquad \text{(II-3a)}$$

where:

$$a_1 = \left[(n_o-n_1)^2 + k_1^2\right]\left[(n_1+n_2)^2 + (k_1+k_2)^2\right] \qquad \text{(II-3b)}$$

$$a_2 = \left[(n_o+n_1)^2 + k_1^2\right]\left[(n_1-n_2)^2 + (k_1+k_2)^2\right] \qquad \text{(II-3c)}$$

$$a_3 = 2\left\{\left[n_o^2 - (n_1^2+k_1^2)\right]\left[(n_1^2+k_1^2) - (n_2^2+k_2^2)\right] + 4n_ok_1(n_1k_2 - n_2k_1)\right\} \qquad \text{(II-3d)}$$

$$a_4 = 4\left\{\left[n_o^2 - (n_1^2+k_1^2)\right](n_1k_2 - n_2k_1) - n_ok_1\left[(n_1^2+k_1^2) - (n_2^2+k_2^2)\right]\right\} \qquad \text{(II-3e)}$$

And the absorption is calculated from:

$$A = 1 - R - T \qquad \text{(II-4)}$$

These equations were solved on a digital computer for films with thicknesses up to 10μ. The calculations were performed at each thickness for the transmission, reflection and absorption coefficients in the region 1μ to 3μ. This band of energies was chosen because it represents the energy associated with from twice down to one-half the bandgap energy of germanium; which corresponds to photons with wavelengths of 1.8μ.

2.3 Absorption in Heavily Doped Germanium

To compute ψ_N the need for the optical absorption of highly doped germanium arose. The author was unable to find published data for germanium doped to a free carrier level of 10^{19} carriers/cm^3. Thus it was necessary to calculate the effect of the carriers on absorption and add this contribution to the intrinsic absorption(8) which was known.

The equation for free carrier absorption for a semiconductor is given by Moss(9) as:

$$\alpha = \left(\frac{\lambda^2 e^3}{4\pi^2 c^3 n \epsilon_o}\right)\left(\frac{N_n}{m_n^{\,2}\mu_n} + \frac{N_p}{m_p^{\,2}\mu_p}\right) \qquad \text{(II-5)}$$

where:

α is the absorption coefficient

λ is the wavelength

e is the charge of an electron

c is the velocity of light in vacuum

n is the index of refraction of media at the calculated wavelength

ϵ_o is the permitivity of free space

N is the free carrier density in the medium

m is the effective mass of the carriers

μ is the carrier mobility

This equation was solved for typical values of constants for germanium and added to the intrinsic absorption to obtain the calculated extrinsic absorption curve.

To solve Equation II-1 we require the index of extinction. The index of extinction is related to the absorption coefficient by:

$$k = \frac{\alpha\lambda}{4\pi} \qquad \text{(II-6)}$$

The calculations for the absorption coefficient contain the index of refraction. The index of refraction is a function of wavelength but Spitzer and Fan(10) have found from experiments with extrinsic germanium that the index of refraction has a constant value of 3.93 in the region from 1μ to 3μ, thus calculations made for the index of extinction in this region will use this value.

Calculated values of the index of extinction and the experimentaly determined values of the index of refraction are contained in Figure II-2.

2.4 Theoretical Results

The equations presented in Section 2.2 were solved with the aid of a digital computer and tabulations of reflection, absorption, transmission, ψ and ψ_N were made for various film thicknesses. Plots of ψ_N versus wavelength for a thickness of 1 and 5 microns were made for the materials which had calculated values of $\psi_N \geq 1$ and are contained in Figure II-3.

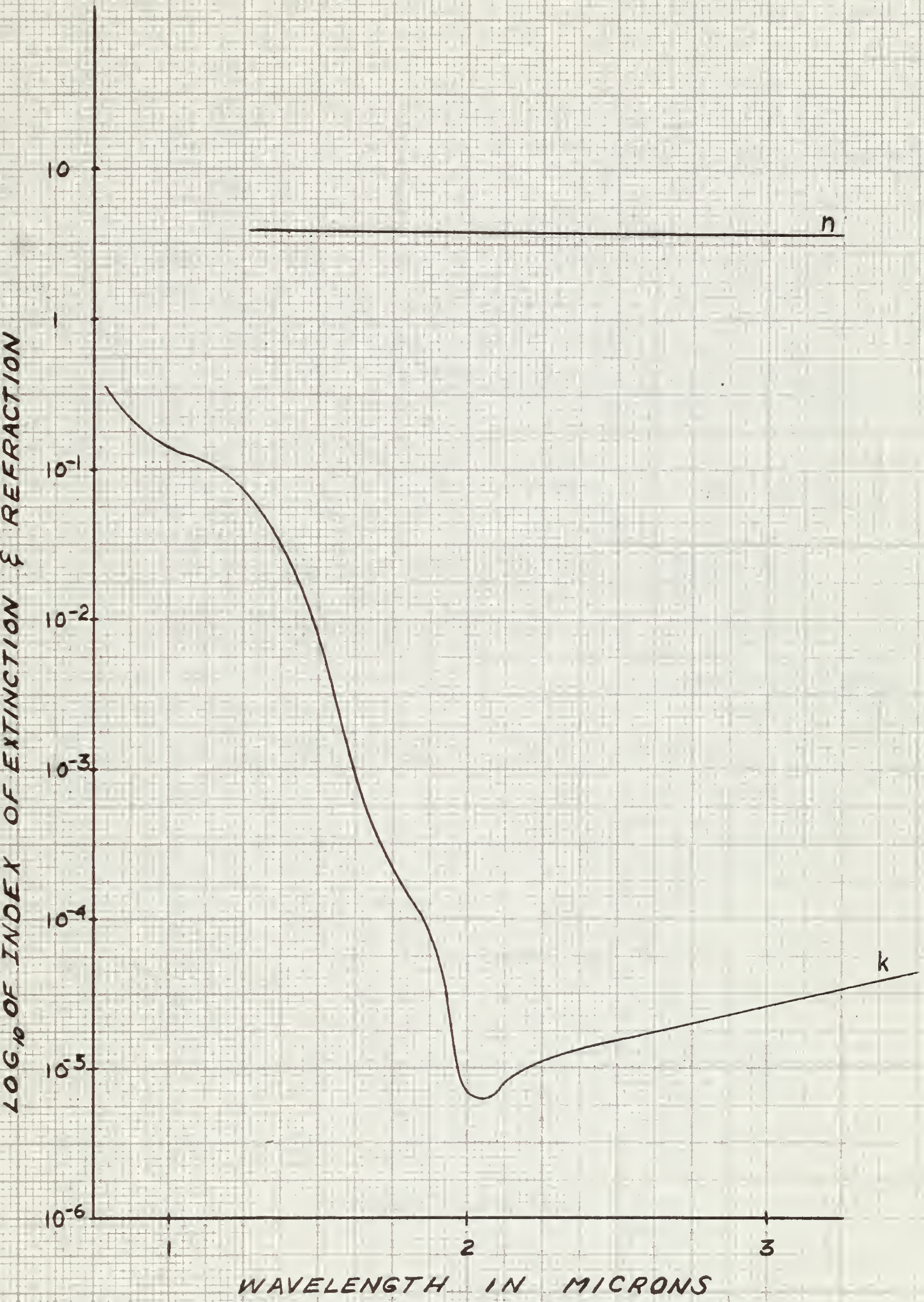


Figure II-2. Calculated Values of Index of Extinction and Experimental Values of Index of Refraction

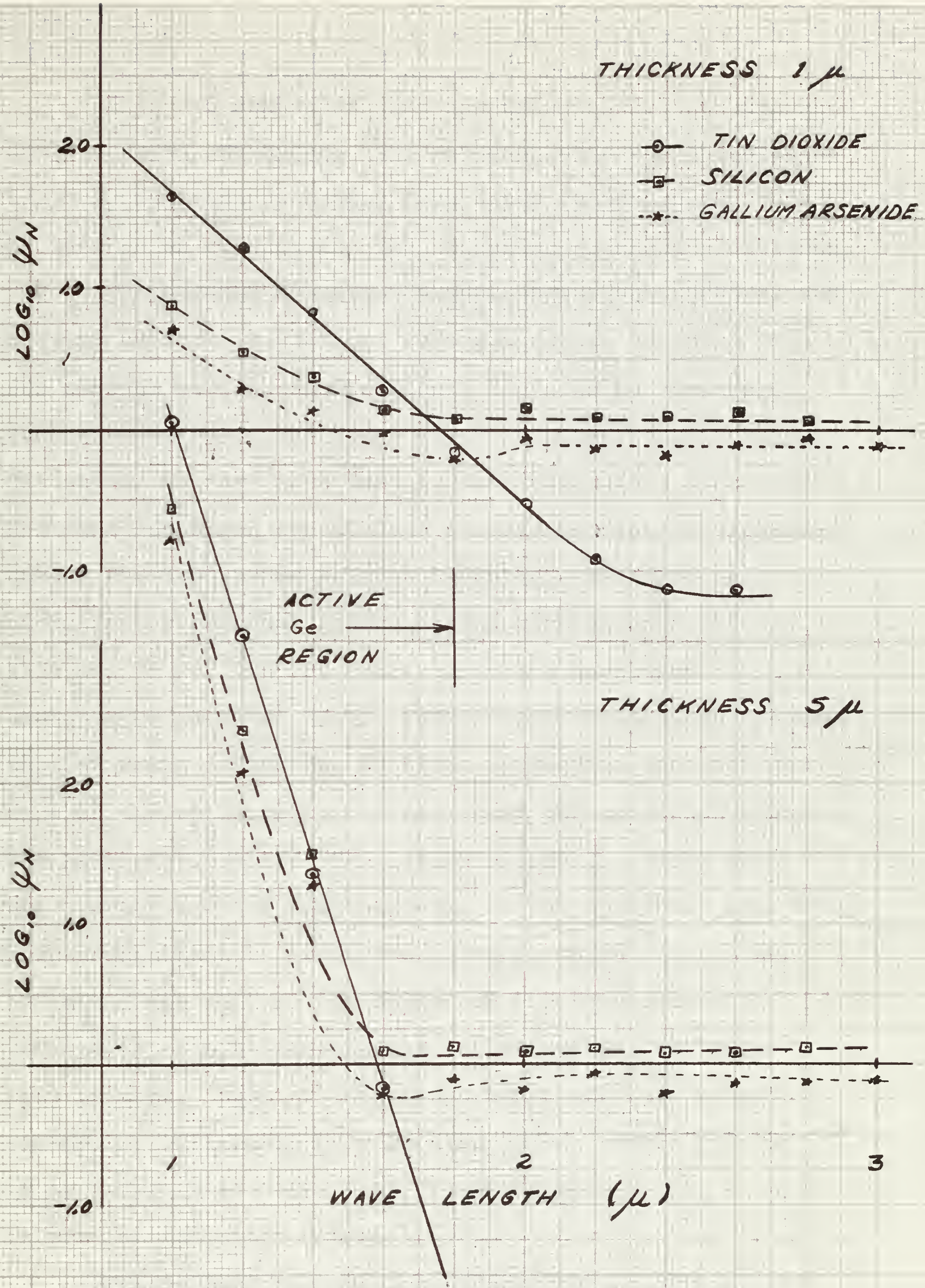


Figure II-3. ψ_N as a Function of Wave Length For Various Investigated Overlay Materials

A $\psi_N = 1$ indicates that the material is the equivalent of doped germanium. Any material with $\psi_N > 1$ indicates that the material is better than doped germanium and could be used as an overlay for the reduction of sheet resistance.

The defined parameter ψ uses only three criteria for a film, as such it will not always indicate the best film for a given overlay application. It is to be remembered that absorption of radiation lower in energy than the bandgap energy is very important in the TPV device, since this incident radiation constitutes a large percentage expected from a thermal source. It is important also that this radiation be returned to the source without undo attenuation at, or in, the TPV cell. The long wavelength radiation can be returned to the source by basically two schemes; that of using reflecting coatings applied to the incident face of the cell, or by reflection of the radiation from the back of the cell. The latter scheme is usable when the overlay and the bulk material of the converter cell are very transparent to long wave lengths, while the former technique may well be the better of the two schemes if the overlay can be made highly reflective to the longer wave lengths. Both of these techniques will aid in system conversion efficiency by returning to the source photons whose energy lies below that of the bandgap energy of the active semiconductor material.

The defined parameter ψ for absorbing films possess a maximum as the sample in Figure II-4 indicates. Data for

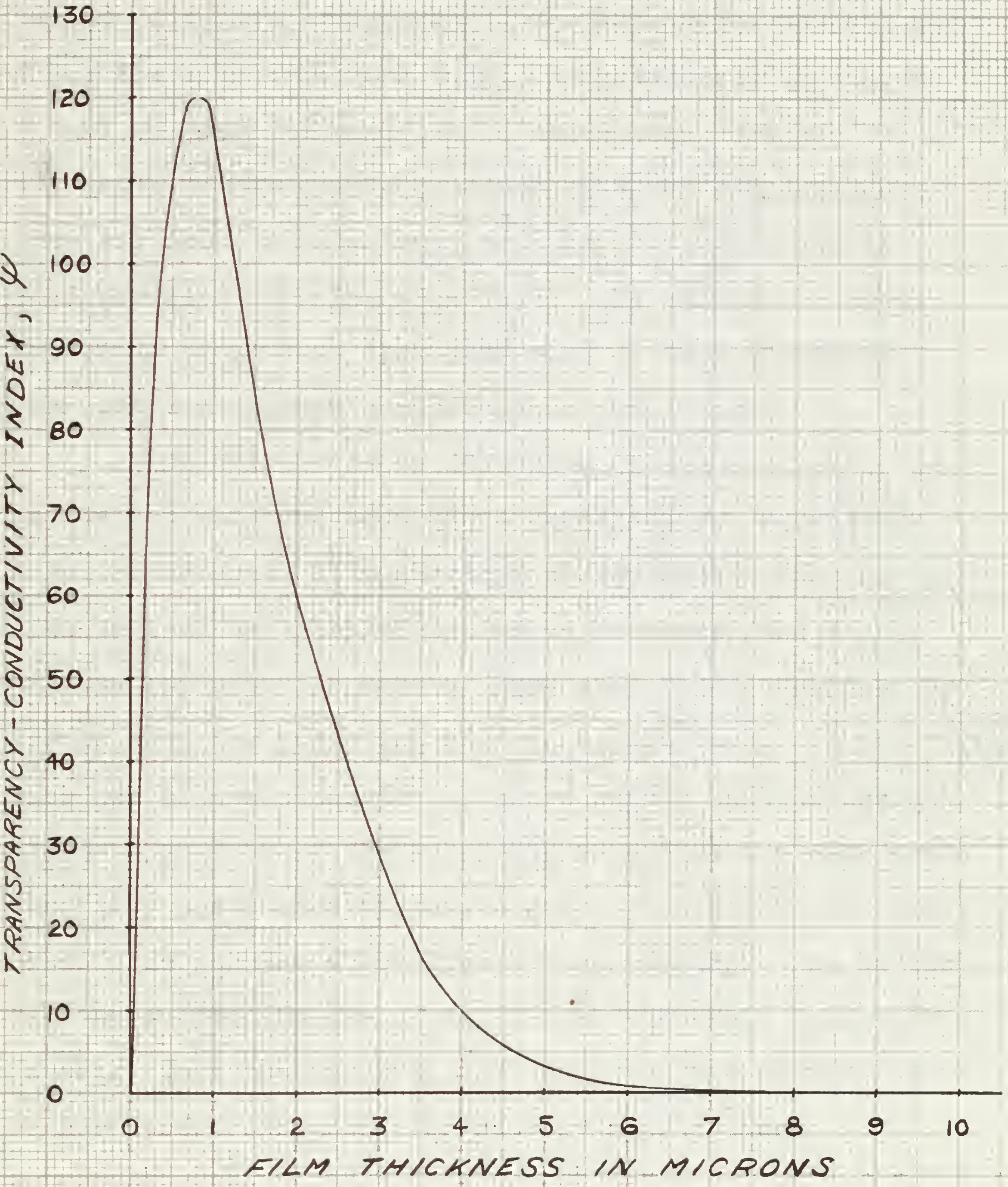
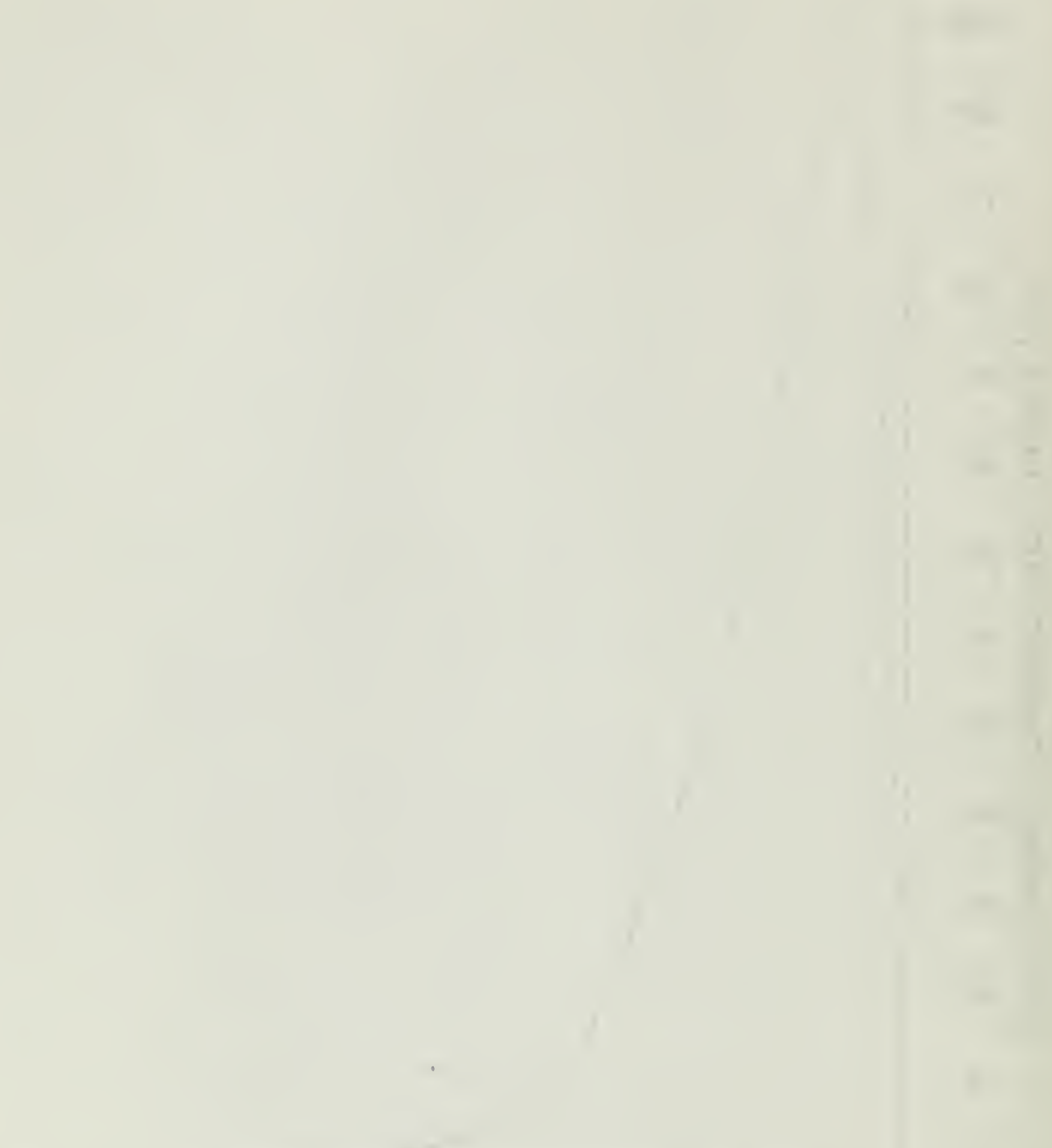


Figure II-4. ψ as a Function of Thickness for Tin Dioxide at a Wavelength of 1.5μ



[illegible]

[illegible]

this sample reported as tabulated in Table II-1 shows that values of ψ_N are continuing to increase while the optimum ψ for the film is around 0.8μ. As previously mentioned, ψ does not use the property of absorption directly for a film and in this sample reliance on $\psi_N > 1$ could produce some erroneous conclusions, because the absorption is 96.3 per cent when Log $\psi_N = 7.36$. The reason for these anomalous results is that germanium is less transparent than the tin dioxide for the given wave length.

Thus while ψ is an indicator of the usefulness of an overlay material to replace germanium for reduction of sheet resistance, it must still be remembered that absorption of long wave length energy is important and either the overlay material must be such that this absorption is low or else the radiation must is bandlimited. In the former case use of semiconductor overlays with a bandgap energy higher than that of the substrate is called for with conductivity controlled by free carrier levels yet with minimized free carrier absorption by the overlay. The latter case calls for the use of multilayer thin film reflective layers. Thus the impurity semiconductor tin dioxide should be further investigated for overlay application.

TABLE II-1

Tin Dioxide Overlay at a Wave Length of 1.5

Thickness	Reflection	Transmission	Absorption	ψ	Log $^{\psi}$N
0.1	.339	.609	.052	32.9	0.86
0.2	.132	.636	.233	68.7	1.01
0.3	.032	.539	.429	87.4	1.05
0.4	.112	.410	.478	88.6	1.06
0.5	.186	.342	.472	92.3	1.10
0.6	.161	.324	.515	105.0	1.19
0.7	.058	.314	.628	119.0	1.30
0.8	.000	.277	.723	120.0	1.36
0.9	.042	.227	.731	110.0	1.40
1.0	.096	.191	.712	103.0	1.44
2.0	.045	.057	.898	61.3	2.12
3.0	.038	.016	.946	26.5	2.78
4.0	.037	.005	.958	10.1	3.43
5.0	.037	.001	.962	3.6	4.09
6.0	.037	.001	.962	1.2	4.74
7.0	.037	.000	.963	0.4	5.40
8.0	.037	.000	.963	0.1	6.05
9.0	.037	.000	.963	0.04	6.71
10.0	.037	.000	.963	0.01	7.36

CHAPTER III

EXPERIMENTAL INVESTIGATION

3.1 Introduction

An experimental investigation of an overlay material to substantiate the theoretical conclusions is necessary to check the validity of the transparency-conductivity index as a criterion for determining the suitability of material for overlay application. Experimental application of tin dioxide will be pursued to determine if the series resistance of a cell can be lowered by applying an overlay. Tin dioxide was chosen because it had a value of $\psi_N > 1$ for a film 1μ thick at a 1.5μ wave length and can be deposited by the following well known techniques:

(a) Cathodic sputtering of tin in a glow discharge containing oxygen, this technique being termed reactive sputtering, and

(b) Producing a pyrolytic reaction between stannic tetrachloride and water vapor.

The deposition of the oxide film from a vapor cloud produced by a chemical reaction between volatile tin chloride and water vapor is currently used for the preparation of transparent conducting tin oxide films on glass(11). The disadvantages of this process are the control of the deposition rate is some what of an art, the film thickness is limited before granularization of the deposited structure

occurs, substrate materials must be heated to high temperatures (about 700°C) and the process must be carried out in a ventilated hood. Advantages of pyrolytic deposition are that no elaborate equipment is used and process times take only a few minutes.

The method of reactive sputtering has several advantages over the pyrolytic technique. After limited experiment, it is usually possible to prepare optically transparent tin dioxide deposits to a specified film thickness. Films of tin dioxide can be deposited by reactive sputtering in tightly adherent homogeneous layers. It is not a requirement of the sputtering process that the substrate be heated to a high temperature, although the substrate may be heated to refine the crystal structure of the deposited film.(12) Disadvantages of sputtering are that elaborate vacuum equipment is necessary and deposition rates are very slow necessitating runs about an hour long.

Conducting films of tin oxide have also been produced by spraying stannic chloride solution in the presence of water vapor onto a hot glass surface. Films produced in this manner have a low resistance of about 50-100 ohms per square* and the optical transmission of about 80 per cent to white light. Gomer(13) has prepared conducting tin oxide films by blowing hot air over stannous chloride crystals. By this technique he succeeded in depositing thick

---

*Ohms per square refers to the resistance that is measured between the opposite edges of a square film of material.

films having resistivities as low as 20 ohms per square, but such thick films were granular and possessed a low optical transmission. Preston(14) has shown that conducting tin oxide films can be prepared by reactive sputtering a partially oxidized tin film of brown body color which becomes conducting when heated in air.

Miloslavskii(15) deposited tin oxide films using the technique of spraying a solution of stannic tetrachloride and glacial acetic acid onto a heated substrate. Antimonic pentachloride was added for increased conductivity. This latter doping technique enabled him to achieve results for correlation of electron concentration and optical density.

It is the results of Miloslavskii's work that caused this investigator to suppose that similar results might be obtained for sputtered films.

The optical density of thin layers of tin dioxide and reflection coefficients for several films are reported in Figure III-1 as an indication of what was to be achieved in the sputtering experiments.

3.2 Cathodic Sputtering

Cathodic sputtering is the process of depositing metal in a near vacuum by a glow discharge. When an electrical discharge is passed between two electrodes in a low gas pressure, the cathode is slowly disintegrated under the bombardment of ionized gas molecules. The disintegrated

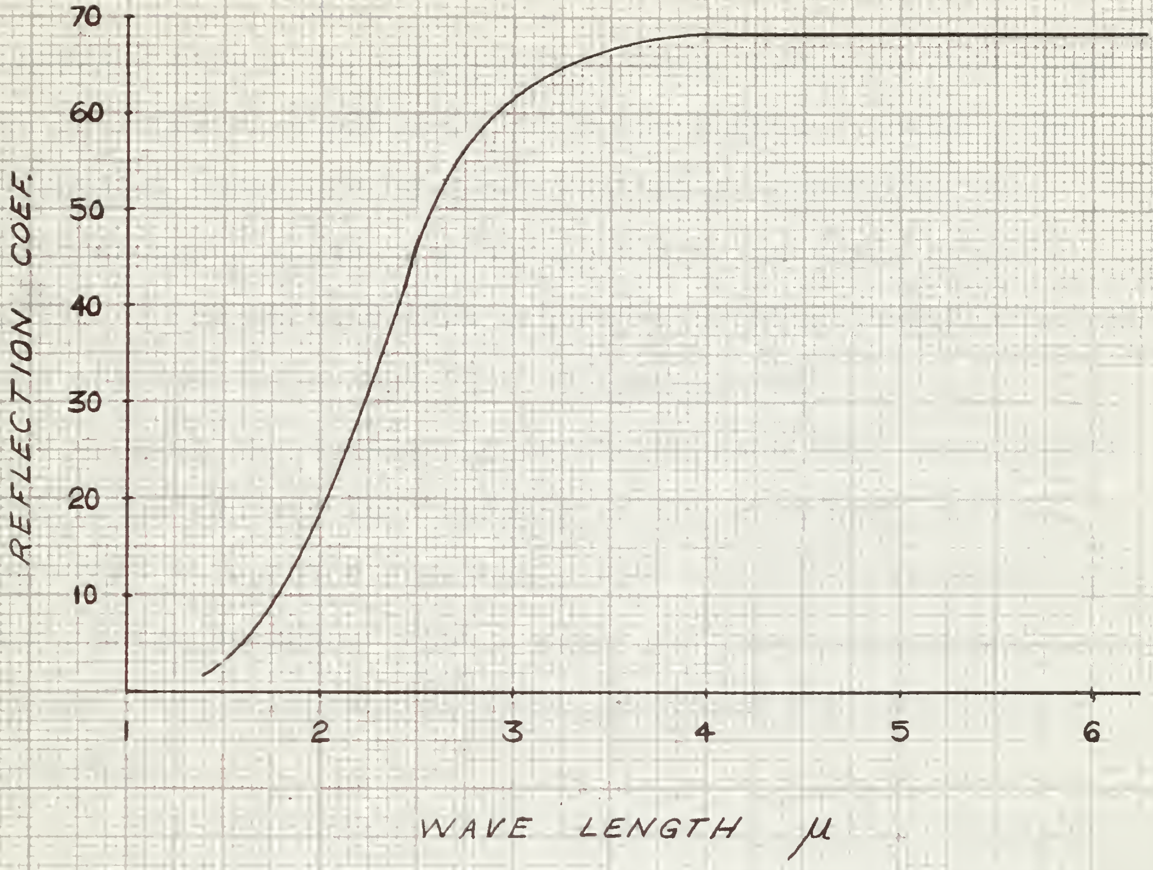
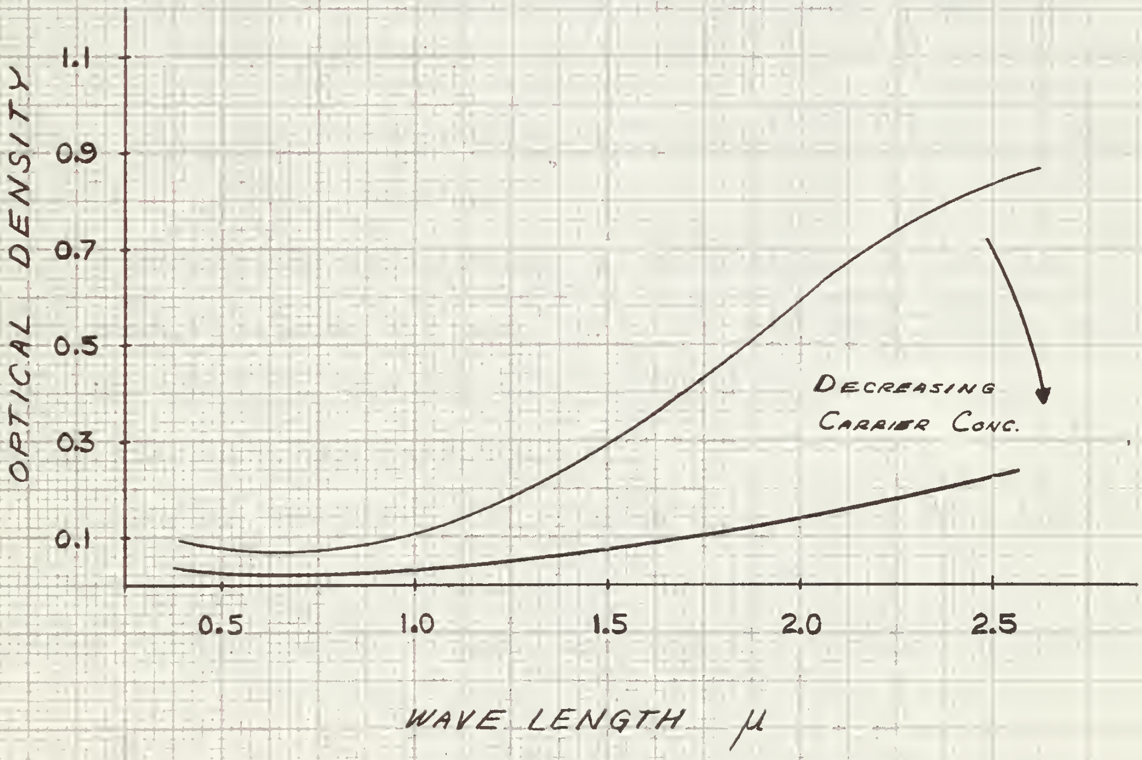


Figure III-1. Optical Density and Reflection Coefficient as a Function of Wavelength for Tin Dioxide



material leaves the electrode surface either as free atoms or in chemical combination with the residual gases. The liberated atoms are condensed on areas surrounding the cathode and a layer of material builds up which is composed of the cathode material and a chemical combination of the residual gases and the cathode material.

Reactive sputtering is the process that uses to the fullest advantage the tendency of the sputtered cathode material to combine chemically with the residual gases in the vacuum chamber. When a metal cathode is sputtered in oxygen the following oxidation processes may occur simultaneously:

(1) Production of an oxide layer on the cathode surface which is removed under positive ion bombardment,

(2) Oxygen absorption by the sputtered atoms in transit,

(3) Oxygen absorption by the sputtered film during its formation.

One of the frustrations of sputtering is the fact that many variables are involved. The gas used, anode-cathode spacing, voltage, current and substrate temperature are among the important variables.

During the first few minutes of a normal run, the temperature in the chamber builds up causing the gas to expand, the pressure to increase, and the current to drop;

therefore, the pressure in the chamber is ignored. By maintaining the current, and hence the number of ions bombarding the cathode constant, reproducible results can more easily be achieved.

The stability of the glow discharge is affected by the anode-cathode spacing. By increasing the spacing, stability over a wider range of voltage-current settings is possible. This stability determines the reproducibility of the tin dioxide films.

The affect of anode-cathode spacing on rate of deposition and the affect of cathode diameter on distribution are variables which are linked because the equipment available to this investigator did not permit cathode diameter variations. Therefore, rate is controllable by anode-cathode spacing alone. Decreasing the anode-cathode spacing increases the deposition rate.

The rate of deposition is controllable by voltage settings when all other variables are fixed. Higher sputtering rates can be obtained by increasing the current. The limiting factor is heating of the substrate.

The graphs contained in Figure III-2 illustrate the functional dependence and interrelationships of the variables discussed in the proceeding paragraphs.

3.3 Experimental Program

The experimental program outlined in this section was

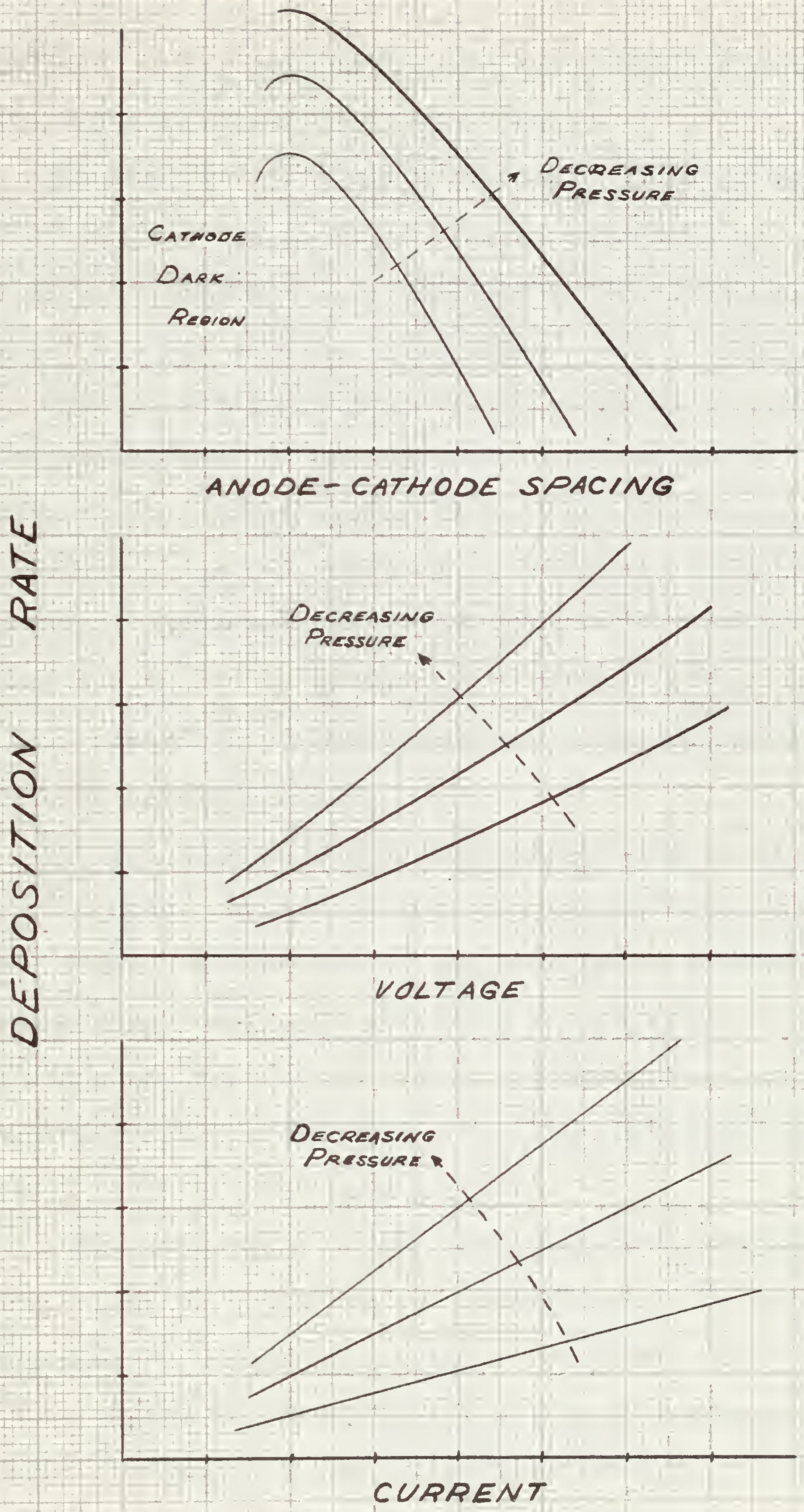


Figure III-2. Functional Dependence and Interrelationships of Sputtering Variables

not pursued to its full extent due to cancellation as a result of the problems mentioned below.

The experiments involved the deposition of thin films of tin dioxide on glass slides. These slides were to be used to determine the thickness, the electrical conductivity and the optical transmission of the deposited film. Optical transmission and reflection of the film were to be measured on an infrared spectrometer for the range 1μ to 3μ. These measured quantities were to be programmed into a digital computer to determine the values of the index of refraction and extinction.(16) A final calculation for ψ_N was to be made to determine if the sputtered film was comparable to the pyrolytically deposited films used in the original calculations.

Several runs at each doping level were to be conducted to insure that representative values were obtained for the films. Effort was to be directed to determining the optimum doping level, as defined by values of ψ_N because it was expected that doping would increase the electrical conductivity but decrease the optical transmission due to changes in free carrier concentration.

Once the optimum doping level had been obtained from experimental analysis, the tin dioxide film would then be deposited on a germanium wafer. The resulting film was to be tested by measuring the change in surface conductivity of the germanium-tin dioxide product. If this

data indicated a reduction in sheet resistance then a thin film of tin dioxide would be deposited on the face of a TPV cell to measure the effect of the overlay on the conversion efficiency of the diode.

The equipment available to the author did not have cathode cooling incorporated into its design. It was first thought that this would not be disadvantageous; however, certain problems arose that made the experimental results less than desired. The application of thin films by cathodic sputtering requires accurate control over the aforementioned variables, and lack of cooling can make this extremely difficult.

It was decided to modify the available equipment so that the tin could be sputtered from the molten state should it melt during the process. This aided to some extent the application of the films that were done. However, the temperature effects were so difficult to overcome that it was necessary to cancel the experiments due to time limitations and lack of free access to equipment.

Although several runs were made using pure tin as the cathode material only one of the samples exhibited any measureable conductivity; however, all the films were quite transparent. Lack of conductivity can be attributed to several causes, but the major one felt to be the culprit in this case was cracking of the film due to thermal stress and subsequent open circuiting. The temperature during the

runs made it difficult to maintain the glow discharge at a steady value and deposition rate varied during the process over quite large values. To produce a film with high conductivity it is necessary that the film be deposited at a very high rate, this goal was not reached during any of the attempts to produce the films that resulted in this experiment.

CHAPTER IV

SUGGESTIONS FOR FUTURE WORK

4.1 Future Work

The development of future work in the application of films by reactive sputtering will require water-cooled equipment similar to that outlined in Appendix A. With the flexibility that is inherent in the design of the outlined equipment it will be possible to produce the films that are needed to determine if sputtered tin dioxide films will produce the necessary reduction in sheet resistance.

During the course of this work it became apparent that other materials were equally available which could aid in the reduction of sheet resistance. Such a film is comprised of boron-doped silicon, data available shows this material to be very useful in the reduction of sheet resistance.(17) Examination of ψ_N for boron-doped silicon substantiates this finding. Silicon when as highly doped as the material used to calculate ψ_N exhibits almost semi-metal properties.

Gallium arsenide is another semiconductor that calculations indicate is suitable if doping does not affect too adversely the optical properties in the 1μ to 3μ region. No accurate data was available for the calculation of ψ_N

for highly doped gallium arsenide, but for the nearly intrinsic compound data(18) was available and is reported as part of Figure II-3.

Not investigated as part of this thesis, but certainly potential materials are very thin films of metals. Gold when deposited in very thin layers has high resistance; however, if gold is deposited on a metal oxide, the resistivity will approach that of the bulk metal when films as thin as 100 Angstrom units are deposited.(19) Calculations for metal as thin as this were not done as it is not certain that the optical properties of the thin metal film remain consistent with the bulk properties.

Finally, it is suggested that further investigation of overlay materials for TPV cells be conducted and that optimization of the conducting overlay with multilayer interference filters for bandlimiting be performed. Also application of very thin films of gold should be performed both on conducting oxides and germanium substrates to determine if values of $\psi_N > 1$ are obtained. Thus it might be possible to obtain improved conversion efficiency by utilizing several thin films which could be fabricated by vacuum production equipment to yield large numbers of units at reasonable cost.

APPENDIX A

SPUTTERING EQUIPMENT OUTLINE

This is an outline of the equipment that would be necessary for the production of reactive cathodic sputtered films of metal oxides. This same equipment could be used for the more conventional application of metal films by sputtering.

The cathodic sputtering process is described in Section 3.2. To support the glow discharge the variables outlined below must be controllable:

(1) Vacuum chamber temperature
(2) Vacuum pressure
(3) Sputtering atmosphere
(4) Anode-cathode spacing
(5) Sputtering current and voltage.

For laboratory application of sputtered metallic films or reactive sputtered films of metallic oxides the same equipment can be utilized as the features of application of these films are the same.

During the potential fall in the glow discharge, energy is dissipated as heat near the cathode. To lessen the effect of temperature as a variable and particularly to prevent melting of either cathode or anode material when low melting point metals or alloys are sputtered, water cooling must be incorporated into plant design. Such water

cooling will also prevent overheating of the vacuum seals and supports during rapid deposition when high voltages and current densities are being applied. The use of water cooling with the high applied voltages is not difficult. It is only necessary that an adequate length of rubber hose be used to keep the leakage current low; under most conditions this amounts to about ten feet.

The gas pressure at which effective glow discharges are maintained is on the order of 10-100 microns. Control of pressure is important as precise control of glow discharge is rendered difficult if pressure fluctuations occur during the sputtering process. For the range of pressure used in sputtering, a mechanical vacuum pump gives erratic performance and a vapor diffusion pump gives more precise control over this range. To this end proper pressure control may then be achieved by bleeding in the sputtering gas mixture via a micrometer valve.

Gas mixtures can be achieved by procuring mixtures from commercial sources. However, for laboratory applications where it may be desirable to alter mixtures and only small quantities are needed in the first place, a mixing chamber may be used. Such a chamber needs to be a pressure flask of about 2-3 cubic feet capacity. The pressure flask should also be fitted for vacuum work. The flask is out-gased along with the sputtering chamber. Mixtures are then obtained by bleeding in the proper gases back in relation to the vacuum-pressure gauge reading. This

process produces excellent mixtures in sufficient quantity for laboratory work.

Another variable which is of frequent use for controlling deposition rates is anode-cathode spacing. This spacing can be varied by incorporating into the upper electrode (anode) a sliding joint platform.

The control of sputtering current and voltage is important to maintain a stable glow discharge and to be able to sputter at very high rates. The laboratory power supply should be capable of voltages up to 5 or 6 kilovolts at a current rating of 500 milliamperes. When high current densities are used, the transition from a glow discharge to an arc discharge can occur quite easily. Should the glow discharge temporarily pass from a limited area of the cathode, due to surface contamination reducing the work function of a particular region, then appreciable local heating of the cathode may take place. This can give rise to thermal emission of electrons which permits the transition from a glow discharge to a high current discharge. To counter this overload demand on the power supply and hence to suppress arcing, reactance limitation of the output current is desirable.

To accomplish these purposes, the proposed design of a laboratory cathodic sputtering equipment is outlined in Figure A-1.

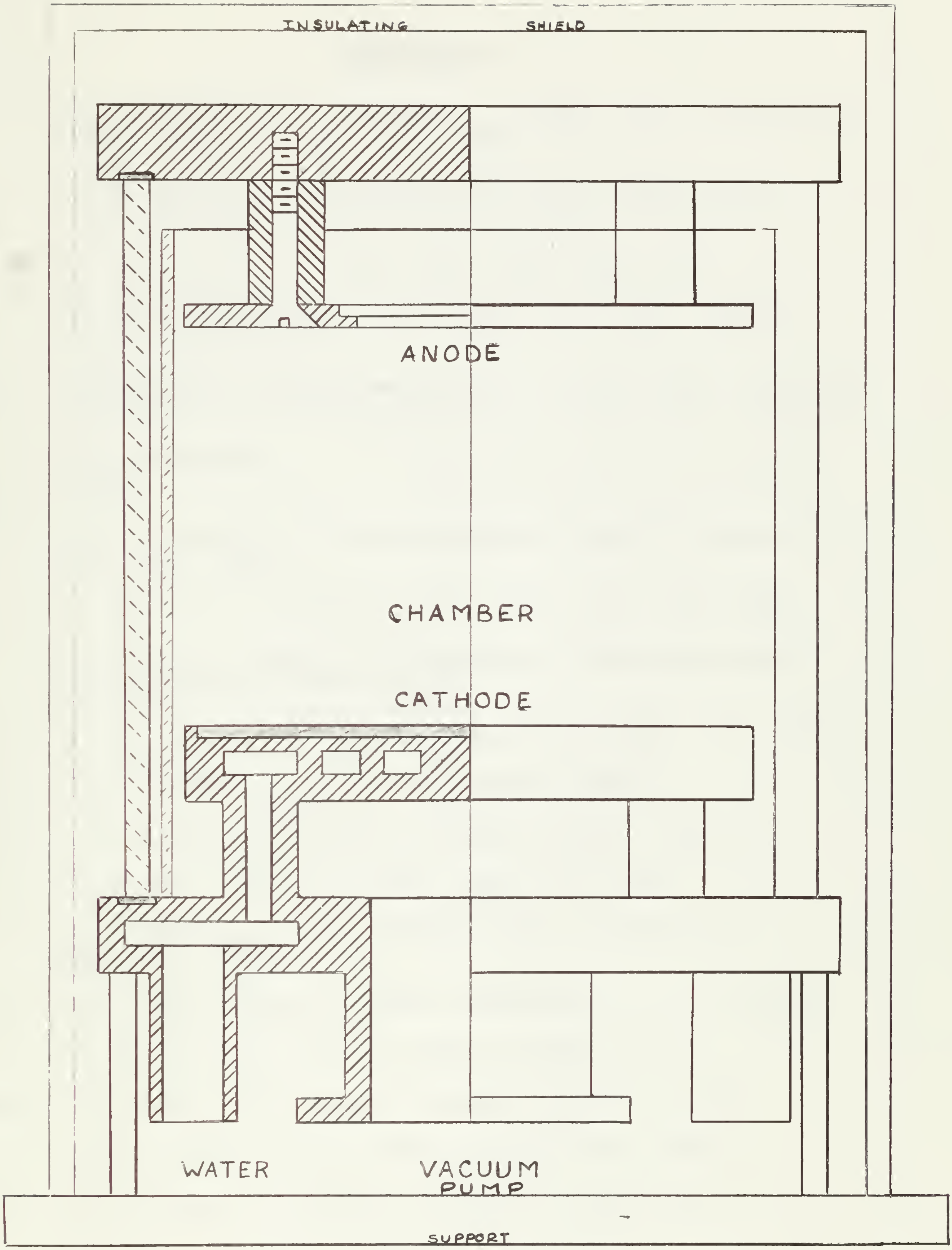


Figure A-1. Cathodic Sputtering Equipment Design

REFERENCES

1. D. C. White, B. D. Wedlock, J. Blair, Proc. 15th Ann. Power Sources Conf., 125, 1961.

2. B. D. Wedlock, Scientific Rpt. No. 3, MIT, Energy Conv. and Semiconductor Lab., 1962.

3. M. B. Prince, J. Appl. Phys., 26, 534, 1955.

4. E. T. S. Appleyard, Proc. Phys. Soc., 49, (Extra Part), E118, 1937.

5. L. Holland, "Vacuum Deposition of Thin Films" Chapman and Hall Ltd., London, 1961.

6. W. H. Brattain, H. B. Briggs, Phys. Rev., 75, 1705, 1949.

7. J. A. Stratton, "Electromagnetic Theory", McGraw-Hill, New York, 1941.

8. W. C. Dash, R. Newman, Phys. Rev., 99, 1151, 1955.

9. T. S. Moss, "Optical Properties of Semiconductors", Butterworths, London, 1951.

10. W. G. Spitzer, H. Y. Fan, Phys. Rev., 106, 882, 1957.

11. J. K. Davis, U. S. Pat. 2,564,677 (1951).

12. L. Holland, G. Siddall, Vacuum, 3, 245, 1953.

13. R. Gomer, Rev. Sci. Inst., 24, 993, 1953.

14. J. S. Preston, E. J. Gillham, Proc. Phys. Soc., 65B, 649, 1952.

15. V. K. Miloslavskii, Optic and Spect., 7, 154, 1959.

16. D. R. Schertz, Thesis, MIT, M.S.E.E., 1961.

17. J. F. Hall, J. Opt. Soc. Amer., 50, 717, 1960.

18. R. E. Morrison, Phys. Rev., 124, 1314, 1961.

19. L. Holland, G. Siddall, Vacuum, 3, 375, 1953.